

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

AeroChem TN-212

DOE/JPL 955491-80/2

Distribution Category:UC-63

(NASA-CR-162871) DEVELOPMENT OF PROCESSES
FOR THE PRODUCTION OF SOLAR GRADE SILICON
FROM HALIDES AND ALKALI METALS Quarterly
Report, 1 Jan. - 31 Mar. 1980 (AeroChem
Research Labs., Inc.) 21 p HC A02/MF A01

N80-22786

Unclas
19284

G3/44

DEVELOPMENT OF PROCESSES FOR THE PRODUCTION OF SOLAR GRADE SILICON FROM HALIDES AND ALKALI METALS

SECOND QUARTERLY REPORT

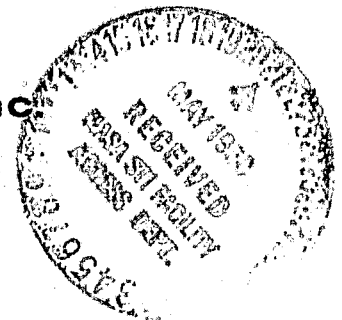
for the Period 1 January to 31 March 1980

C. R. DICKSON AND R. K. GOULD

APRIL 1980

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DoE.

AeroChem Research Laboratories, Inc.
Princeton, New Jersey



This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ABSTRACT

This program is directed toward the development of processes involving high temperature reactions of silicon halides with alkali metals for the production of solar grade silicon in volume at low cost. Experiments are being performed to evaluate product separation and collection processes, measure heat release parameters for scaling purposes, determine the effects of reactants and/or products on materials of reactor construction, and make preliminary engineering and economic analyses of a scaled-up process. Samples of the silicon product will be delivered to JPL for evaluation of solar cell performance.

During this reporting period, the program efforts were directed toward the measurement of reagent flow rates and silicon collection efficiencies, the construction of a new sodium heat pipe to permit one to two hour runs, and the completion of the economic and engineering analyses of the AeroChem process to make solar grade silicon. At standard operating conditions the sodium flow rate was found to be $0.36 \pm 0.04 \text{ g s}^{-1}$ and the SiCl_4 flow rate was found to be $0.72 \pm 0.03 \text{ g s}^{-1}$. This corresponds to a Na/ SiCl_4 molar ratio of 3.7, a nearly stoichiometric ratio slightly rich in SiCl_4 . At these flows, the total rate of Si production is $0.4 \text{ kg of Si h}^{-1}$. In 15 to 20 minute Si production runs samples of metallic silicon (up to 80 g) were collected at high separation/collection efficiencies ($\approx 60\text{--}80\%$) using alumina and POCO DFP1 graphite crucibles at 1650 K. The length of these runs was limited by the Na supply. The silicon produced contained less than 10 ppm Na impurity. The new high capacity Na vaporizer is completed, installed, and operational. The first successful run lasted $1 \frac{1}{4}$ h during which time 238 g of silicon were separated at an 82% efficiency. The preliminary economic and engineering analyses have determined that the cost of silicon made by the AeroChem process would be $\$10.18 \text{ kg}^{-1}$ in 1980 dollars for a 1000 MT yr^{-1} plant. For 20% ROI, after taxes (46%), the estimated price would be $\$13.15 \text{ kg}^{-1}$.

DRL No. 118
Item No. 4, DRD No. QR

DOE/JPL 955491-80/2
Distribution Category:UC-63

DEVELOPMENT OF PROCESSES FOR THE PRODUCTION OF SOLAR GRADE SILICON FROM HALIDES AND ALKALI METALS

SECOND QUARTERLY REPORT
for the Period 1 January to 31 March 1980

C. R. DICKSON AND R. K. GOULD

APRIL 1980

JPL Contract No. 955491
LSA Task 1, SILICON MATERIAL

Approved by 

Hartwell F. Calcote
Director of Research

AeroChem Research Laboratories, Inc.
Princeton, New Jersey

FOREWORD AND ACKNOWLEDGMENTS

During this report period A. Wilczynski and P.J. Howard contributed to this program.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
I. INTRODUCTION	1
II. TECHNICAL DISCUSSION	2
A. Reagent Flow Rate Measurements	2
B. Silicon Separation/Collection Efficiency	3
C. Materials Study	4
D. Silicon Product	5
E. New Sodium Vaporizer	7
F. Engineering and Economic Analyses	9
III. PLANS	17
IV. NEW TECHNOLOGY	17
V. REFERENCES	17

LIST OF TABLES

<u>Table</u>		
I	EMISSION SPECTROGRAPHIC ANALYSIS OF SILICON SAMPLES	6
II	RAW MATERIAL REQUIREMENTS	12
III	UTILITIES REQUIREMENTS	13
IV	TOTAL PRODUCT COST ESTIMATION	16

LIST OF FIGURES

<u>Figure</u>		
1	NEW SODIUM VAPORIZER	8
2	PROCESS FLOW SHEET FOR AEROCHEM PROCESS	10

PRECEDING PAGE BLANK NOT FILMED

I. INTRODUCTION

The object of this program is to determine the feasibility of using continuous high temperature flames of alkali metals and silicon halides to produce high purity "solar grade" silicon in large quantities. These flames have been observed previously¹⁻⁶ and were found to be characterized by fast kinetics and a variety of chemiluminescent emissions. Equilibrium thermochemical calculations⁴ indicate that high adiabatic flame temperatures (≈ 2400 K) are attained and that solid or liquid silicon is the only condensed phase present in the equilibrium product distributions at these temperatures. Thus, separation of the condensed silicon from the gas-phase reaction products offers the potential for a large scale industrial process for the preparation of high purity "solar grade" silicon.

The present process⁷ has several distinct advantages. Before mixing in the reactor, both reagents are vaporized, thereby contributing to a purer silicon product. The enthalpy of vaporization that would normally be lost in a separate distillation process for reagent purification can, in this configuration, contribute to maintaining the high temperatures in the post-flame gases necessary for product separation. Also the product separation may be a purification process since impurities may be carried away with the salt vapor instead of condensing with the silicon. Finally, little inert gas diluent is required (or desired) in these diffusion flames which results in an obvious economic advantage.

The aims of this program are to achieve product separation, to test various reactor-collector designs, and to run the silicon test apparatus for extended periods of time. During this reporting period, the silicon test apparatus was run repetitively on a routine basis for periods of twenty minutes, until all of the sodium reagent in the vaporizer was depleted. These runs enabled us to measure the reagent flow rates and the silicon collection efficiencies. Samples of metallic silicon weighing 50 to 80 g were collected by an impaction process⁷ at efficiencies of 60 to 80%. This was especially encouraging since complete product separation was demonstrated. Unlike the separation achieved previously³ in a graphite flow tube, the silicon separated by impaction produced only metallic-like silicon ingots with no visible evidence of the powdered product. Analysis of these samples by plasma emission spectroscopy showed the sodium content to be less than 10 ppm.

Also during this reporting period, a new large capacity (3 kg) Na vaporizer was constructed, installed, and put into operation. The first successful run lasted 1 1/4 h and produced a 238 g of separated silicon at an 82% collection efficiency. Finally, the preliminary economic and engineering analyses of the AeroChem process were completed and the cost of the silicon product was estimated to be \$10.18 kg⁻¹ in 1980 dollars for a 1000 MT yr⁻¹ plant.

II. TECHNICAL DISCUSSION

A. REAGENT FLOW RATE MEASUREMENTS

To ensure that the silicon reactor is operating near stoichiometry, the reagent flow rates were measured for simulated (no reaction taking place) and actual running conditions. For the production of 0.5 kg h⁻¹ Si, the SiCl₄ flow rate must be 0.84 g s⁻¹ and the Na flow rate must be 0.46 g s⁻¹. The SiCl₄ flow rate was measured by monitoring the volume loss in the SiCl₄ heat pipe reservoir. These volume measurements were accurate to within 1%. The sodium flow rate was measured by simple weight loss of the sodium vaporizer (≈5 kg) which can be weighed to within 0.01% uncertainty, but oxidation during heating, and sodium leakage at the valve result in a ≈5% uncertainty in the Na flow rate.

No reaction took place during the simulated run, and each reagent flow rate was separately measured. The operating conditions were 12 psig in the SiCl₄ vaporizer with a 0.041 in. diam orifice and 0.5 atm pressure in the Na vaporizer having a 0.125 in. diam orifice. Both reagents expanded sonically into the process vessel held at a pressure of 0.1 Torr. During actual runs, these operating conditions cannot be kept perfectly constant because of pressure and temperature variations as the reagents are depleted. The results of the simulated runs gave flow rates of 0.72 g s⁻¹ for SiCl₄ and 0.5 g s⁻¹ for Na. This is a Na/SiCl₄ molar ratio of 5.5 (4 is stoichiometric). However, for three actual runs, the Na flow rate measured 0.36 ± 0.04 g s⁻¹ and the SiCl₄ flow rate measured 0.72 ± 0.03 g s⁻¹. This corresponds to a Na/SiCl₄ molar ratio of 3.7, a nearly stoichiometric ratio slightly rich in SiCl₄.

For all of the reactor variations tested thus far, both the mixing and reaction appear to be completed within the confines of the 0.58 l reactor assembly. Otherwise, molecular chemiluminescence or Na^{*} emission would be

observed outside the immediate vicinity of the collection vessel. Other evidence for the completeness of the reaction is that the process vessel pressure does not increase with the vacuum pump shut off.

B. SILICON SEPARATION/COLLECTION EFFICIENCY

The basis for continuous product separation is that the alkali metal salt exits as a gas from the reaction chamber while the silicon product is present as a condensed phase. As the products exit from the reactor nozzle, a shock wave is formed upon impaction on the collecting crucible which is kept at a temperature near 1700 K. The salt vapor flows away from the crucible, leaving much of the condensed silicon behind.

Earlier in this program, product separation by impaction was demonstrated and consolidated metallic silicon samples were obtained. However, the collection efficiency of this separation process must also be measured, since it represents an important factor in the economic analysis. Because 98-99% of the silicon is formed in the condensed phase in the post-flame region and very large pressure drops are available for the impaction process, we previously anticipated that this collection efficiency should be high.

For each of the runs made during this reporting period, the weight of Na and SiCl_4 consumed and the weight of the silicon produced were measured. An efficiency of the collection process was estimated by computing the ratio of the actual Si collected to the total weight of Si produced.* At temperatures 50-100 K above the melting point of silicon (≈ 1690 K) nearly all of the silicon produced was deposited with the salt byproduct on the walls of the process vessel, i.e., virtually no product separation occurred. At temperatures slightly above the melting point of silicon, the collection efficiencies measured ≈ 30 to 40%. At temperatures at or slightly below the melting point of silicon, the collection efficiencies measured 60 to 80%. The highest efficiencies measured thus far, including the 1 1/4 h run, have been 82%. All of these efficiencies were measured in runs using a simple pedestal impactor in the collection crucible. The above observations indicate that the collection efficiency is a strong function of collector temperature.

* In each run some of the silicon produced soaks into the graphite reactor. This silicon is counted as collected silicon.

One explanation that could account for the temperature dependence of the collection efficiency is that the silicon aerosol particulates coalesce and increase in size near the impactor surface which is at a temperature below the melting point of silicon. These larger aerosol particles then aggregate upon impaction into a silicon mass more easily than smaller particles. The formation of the larger silicon particles is similar to the formation of fog when warm air passes over a cold surface and the silicon mass is analogous to the formation of "ice feathers" which grow toward the wind at very cold temperatures during winter months.

Other factors such as collector geometry, collector-nozzle exit distance, and nozzle diameter could also be important in optimizing the collection efficiency. A systematic study of the effects of each of these parameters would be valuable but is well beyond the scope of this program. Furthermore, since high separation efficiencies are now being obtained regularly, there is less urgency in finding ways of further improving the efficiency, and research in other problem areas (purity and long run times) will be emphasized in the remainder of the program.

C. MATERIALS STUDY

Several attempts were made to collect large samples of silicon as cast ingots. The failure of the materials initially used as collection vessels frustrated these attempts. Quartz collection dishes withstand the attack by silicon but either the SiCl_4 , NaCl , or Na attacks the quartz dish at temperatures of 1700 K. To investigate alternative crucible materials, samples of sintered SiC (from Carborundum Co.) were placed in the Na vaporizer, reactor chamber, and collection vessel. All samples remained completely unchanged. Thus, sintered SiC may prove to be a suitable material for the reactor-collector assembly.

Several other alternative materials were tested as collection crucibles for the silicon product. A tantalum dish at 1800 K was completely destroyed during a twenty minute run and no silicon was collected. Using an alumina crucible at 1650 K, it was possible to successfully collect the silicon. Crucibles made from POCO DFPI graphite, which the manufacturer reputed to be highly impervious, did not contain the silicon at 1800 K. However, at 1650 K no silicon was observed to penetrate the POCO DFPI graphite and a consolidated,

metallic silicon sample was successfully collected. More silicon was produced than could be contained by either the alumina or graphite crucibles ($\approx 20 \text{ cm}^3$ capacities) and both vessels overflowed during the course of the twenty minute runs.

D, SILICON PRODUCT

Because large samples of silicon were obtained in this reporting period, it was possible to begin to characterize and evaluate the silicon product as a potential solar grade feedstock material. The silicon obtained was analyzed and evaluated with respect to its crystalline nature, electrical properties, and purity. These results are presented here.

The silicon obtained by the AeroChem process appeared as a consolidated polycrystalline mass. One silicon ingot was sliced into 1 in. diam wafers using a diamond saw. Microscopic examination of the wafers after polishing and etching revealed irregularly shaped crystals of silicon that were often several mm long. Several small (0.3 mm) triangular faces of {111} planes of single crystals were identified. On one ingot two hexagonal shaped faces of single crystals were observed. The length of a diagonal in these hexagons measured $\approx 4 \text{ mm}$.

The resistivity of the polished and etched wafers, as measured by the four probe resistivity technique, varied from values of several hundred $\Omega\text{-cm}$ to $\approx 1000 \Omega\text{-cm}$. These resistivity values may have some meaning in spite of the polycrystalline nature of the silicon since the resistivity was lowered to less than $10 \Omega\text{-cm}$ by doping one of the wafers with boron. The silicon material was found to be p-type using the hot probe technique. This result is consistent with the 3 ppm impurity level of Al found in this particular sample of silicon.

The silicon samples collected in the graphite and alumina crucibles were subjected to semi-quantitative analysis by emission spectroscopy. In addition, the sodium levels for both samples were measured quantitatively by plasma emission spectroscopy. Only the results of the analysis of the silicon collected in the alumina crucible are available at this time. This analysis is presented in Table I and is to be compared with the analysis of silicon samples collected three months earlier. The early run shows levels of several impurities that are detrimental to solar cell performance. However, the March

TABLE I
EMISSION SPECTROGRAPHIC ANALYSIS
OF SILICON SAMPLES

<u>ELEMENT</u>	<u>MARCH RUN IMPURITY CONC. ppm</u>	<u>DECEMBER RUN IMPURITY CONC. ppm</u>	<u>DETECTION LIMIT (min. conc.) ppm</u>
Ag	<1	5-10	1
Al	3	200	1
As	nd	nd	300
B	nd	10	10
Ba	nd	nd	300
Be	nd	nd	10
Bi	nd	nd	10
Ca	nd	100	1
Cd	nd	nd	30
Co	nd	nd	10
Cr	nd	150	10
Cu	nd	150	1
Fe	nd	150	10
Ga	nd	nd	10
Ge	nd	nd	10
In	nd	nd	10
Mg	1-10	80	10
Mn	nd	nd	10
Mo	nd	nd	10
Na	nd(10) ^a	500	300(5) ^a
Ni	nd	1000	10
P	nd	nd	100
Pb	nd	nd	30
Sb	nd	nd	100
Sn	nd	nd	10
Ti	nd	nd	10
V	nd	nd	10
Zn	nd	nd	100
Zr	nd	nd	10

^a Plasma emission spectroscopic analysis gave 8-10 ppm Na for the March run. The limit for this technique is 5 ppm.

IN-212

run shows only 1-10 ppm Mg, 3 ppm Al, and less than 1 ppm Ag. All other impurities were below the detection limit for emission spectroscopy. The source of Al and Mg may be the alumina collection dish or the alumina SiCl_4 inlet. The source of Ag is probably the stainless steel fittings used in the sodium and SiCl_4 delivery systems which use an Ag coating to prevent galling.

The December run lasted only three minutes while the duration of the March run exceeded twenty. Thus, the longer runs appear to reduce the impurity levels. Consequently, the one to two hour runs may produce extremely pure silicon product. When no major impurities can be detected by emission spectroscopy, samples will be submitted to JPL for evaluation.

Since sodium is used to produce the silicon product in the AeroChem process, the samples were subjected to a more quantitative analysis by plasma emission spectroscopy. For the samples collected in graphite and alumina crucibles, the sodium level was less than 10 ppm. This is a significant improvement from the 500 ppm level found in the early run last December. The testing laboratory performing the analysis believes that the sodium level is most likely not from the silicon sample itself but from ever-present contamination sources even during careful analysis. Thus, residual amounts of sodium in the silicon product do not appear to be a problem in the AeroChem process.

E. NEW SODIUM VAPORIZER

Prior to this reporting period the silicon test apparatus could only be run for periods of twenty minutes. This limitation is due to the capacity of the sodium vaporizer. An attempt to run longer by over-filling the vaporizer resulted in liquid sodium entering the apparatus and promptly destroying many graphite components. Consequently, it is essential to have a vaporizer with a large separate reservoir that can replenish the sodium consumed during operation. In this reporting period a new large capacity (≈ 3 kg) Na vaporizer was constructed. This larger capacity permits longer runs (1-2 h) and results in larger (0.25 - 0.5 kg) silicon samples.

A diagram of the new large capacity sodium vaporizer is shown in Fig. 1. The sodium in the 3 kg reservoir is melted or solidified by using hot oil or cold water coils which are silver-soldered to the reservoir. The liquid sodium flows by gravity through a 3/8 in. diam stainless steel tube into the

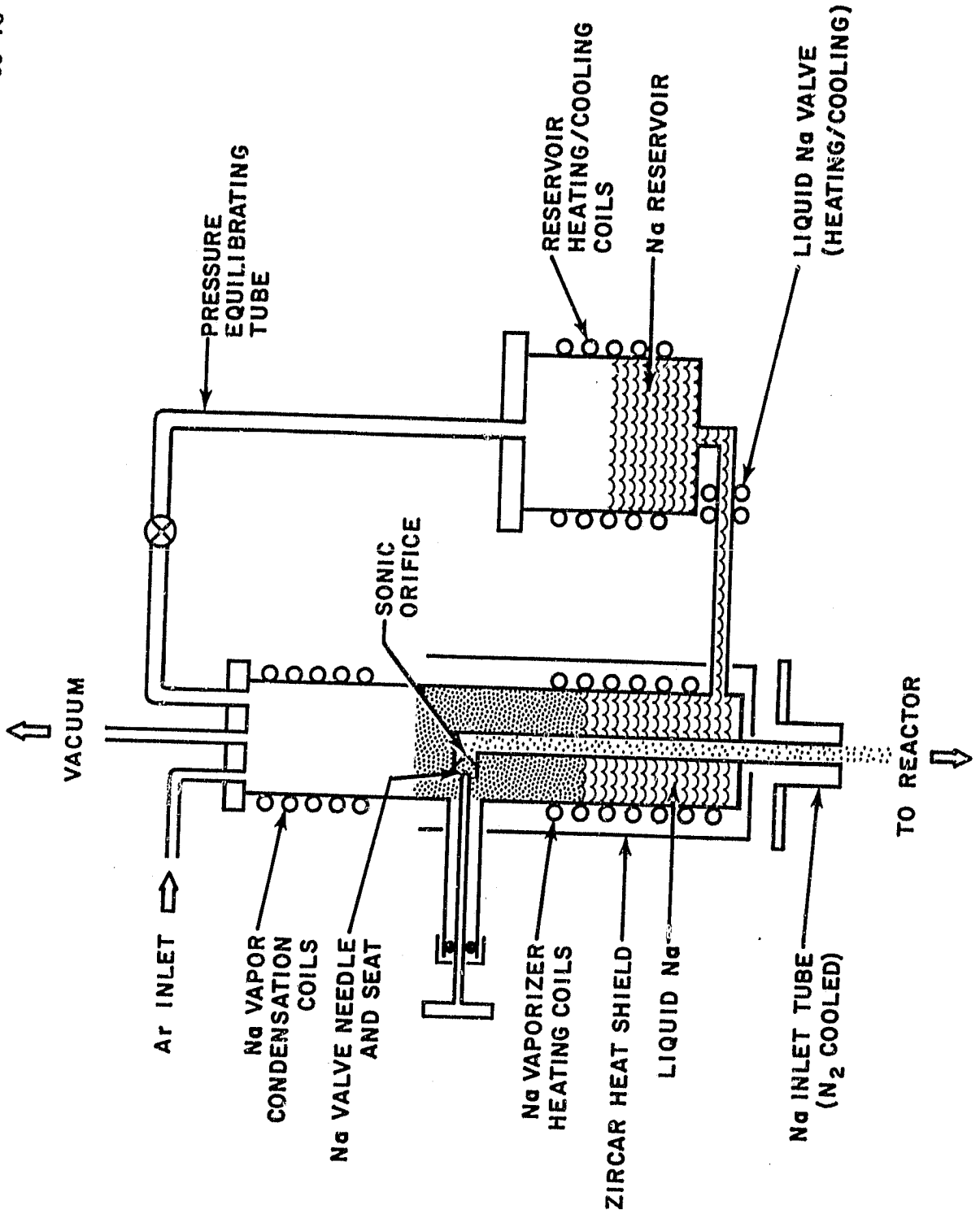


FIGURE 1 NEW SODIUM VAPORIZER

sodium vaporizer. A pressure equilibrating tube maintains equal pressures in the vaporizer and reservoir during filling. When the valve in the pressure equilibrating tube is closed, the sodium can be forced back into the reservoir by pressurizing the heat pipe with argon. The liquid sodium is "valved off" with a cold water coil producing a plug of solid sodium in the vaporizer inlet tube. The valve is opened by melting the solid sodium plug with a hot oil coil.

The Na vaporizer is similar in design to the vaporizer described previously with two major differences. First, hot oil coils instead of cold water coils condense the sodium vapor. This prevents clogging by solid sodium since the oil is kept above the Na melting point. Second, the valve needle and seat are inside the vaporizer and are thus surrounded by the Na vapor. This keeps the orifice and the inlet tube at the boiling point of Na and prevents clogging.

The remaining features of the new large capacity Na vaporizer are identical with only minor modifications. The liquid sodium is vaporized by resistively heating a 3/16 in. diam stainless steel coil. The sodium vapor expands sonically through a 0.09 in. diam orifice into the Na inlet tube leading to the reactor. Flowing N₂ gas prevents melting of the inlet tube and oxidation of the stainless steel heating coil. The vaporizer insulation is made from alumina.

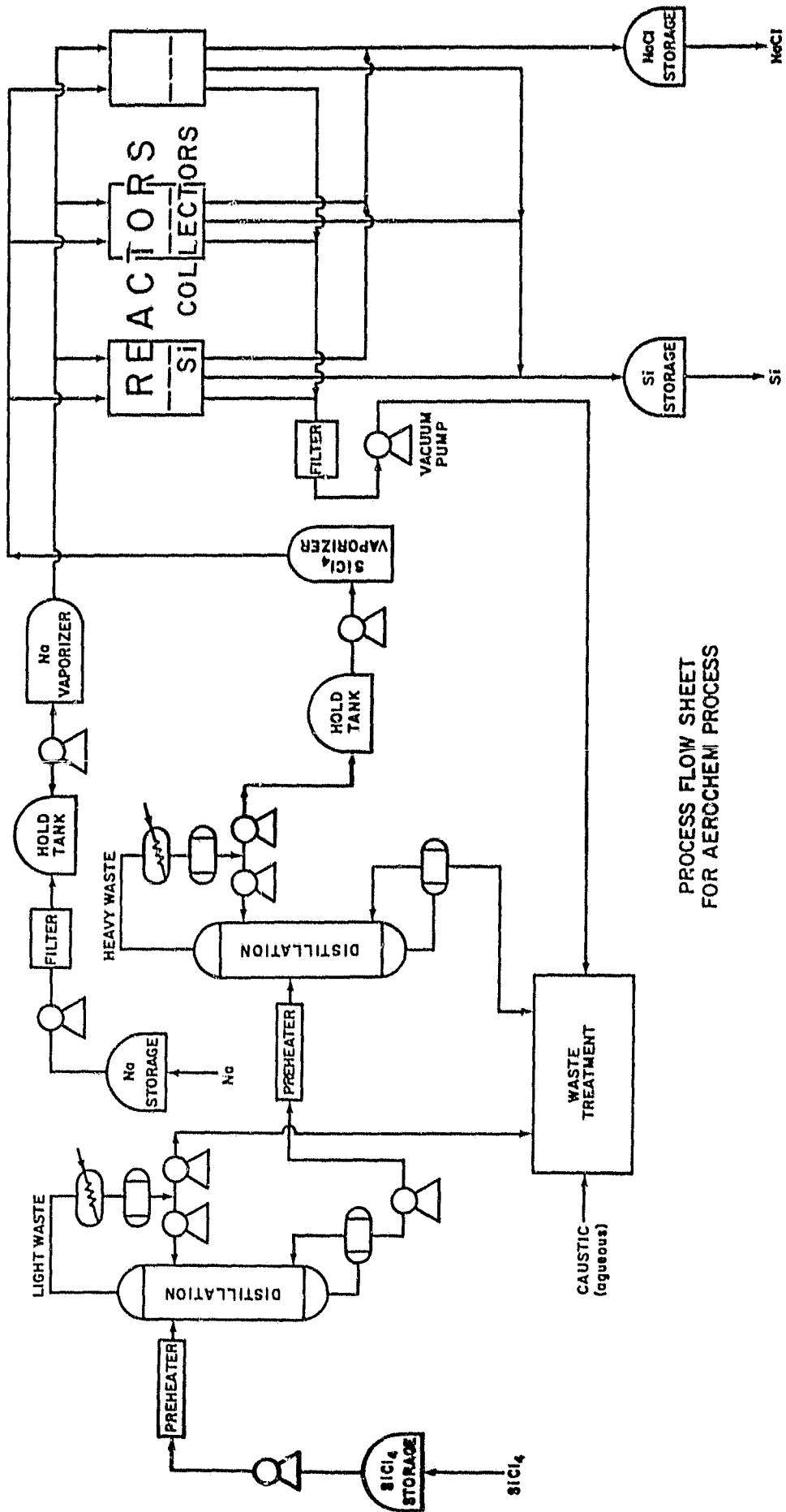
We have eliminated several small difficulties encountered in initial testing of the new vaporizer and have developed safety procedures for handling large quantities of liquid sodium. The system is now operational and has been successfully run for 1 1/4 h.

F. ENGINEERING AND ECONOMIC ANALYSES

Preliminary economic and engineering analyses for the AeroChem process were completed in this reporting period. The cost estimate for production of silicon is \$10.18 kg⁻¹ silicon. The analysis presented here follows closely the analysis of the Battelle process given by Dr. Carl Yaws at the 13th PTM (see also Ref. 8). The cost estimate determined for the AeroChem process is based on the following:

- (i) The costs described here are for a 1000 MT yr⁻¹ demonstration plant.
- (ii) The costs are in terms of 1975 dollars. To arrive at 1980 dollars, the 1975 dollars are multiplied by 1.4.
- (iii) Prices for raw materials are taken from the January 1975 Chemical Week Report.

80-49



PROCESS FLOW SHEET
FOR AEROCHEM PROCESS

FIGURE 2 PROCESS FLOW SHEET FOR AEROCHEM PROCESS

- (iv) Labor costs and utilities rates are those used in Yaws' Battelle analysis.
- (v) Other items in obtaining the cost per kg of silicon are based on these basic costs and are obtained using Yaws' multiplication factors.
- (vi) Finally, the cost of major equipment at the present time relies heavily on comparison with similar equipment used in the Battelle process. Scaling of equipment costs is done using a 0.6 exponent. Our major uncertainties at this time lie in the estimation of costs of some of these items, particularly the reactors.

The AeroChem process, as now envisioned, consists of (i) purification and vaporization of SiCl_4 , (ii) vaporization of sodium metal, and (iii) reaction of SiCl_4 and sodium vapor, and collection of silicon (in 0.5 g pellets) and NaCl (in pellet or small ingot form). A flow chart for the AeroChem process is shown in Fig. 2. No electrolysis of the salt to recover sodium is currently considered. The reasons for this are: (i) it complicates the process dramatically, (ii) first-cut cost estimates show an actual cost disadvantage in doing so, (iii) talks with sodium manufacturers are discouraging as to the practicality of doing salt electrolysis on this small a scale for reasonable costs, and (iv) since all sodium is currently made electrolytically it tends to be reasonably pure (calcium is the major impurity).

The raw materials required for the process are shown in Table II. We have assumed that 90% of the silicon produced is collected. (In our most recent run 82% of the silicon produced was collected so this is not an unreasonable goal.) The rest is assumed mixed with the salt byproduct and thus lost. The reactor is assumed to be run with slight (1-3%) excess SiCl_4 to avoid having to treat and dispose of unreacted sodium. The thermodynamic efficiency is greater than 99% at stoichiometry but some additional losses (1 to 3%) of SiCl_4 are assumed in the 5% loss figure (item 1.d. of Table II). No SiCl_4 would be recycled and the salt byproduct carrying with it 10% of the silicon will be disposed of with no financial gain or loss. From our most recent results these estimates appear conservative; the amount of SiCl_4 needed may well be 5% less than that quoted (15.8 lb instead of 16.7 lb).

In Table III the utilities requirements are described. The major power requirement (6.1 kWh/(kg of Si)) is for the sodium vaporization process. The steam requirements (2.a.) are obtained from Yaws' Battelle analysis by

TABLE II
RAW MATERIAL REQUIREMENTS

<u>Material</u>	<u>Cost/kg of Si</u>
1. SiCl ₄ , 16.692 lb/kg at \$0.135/lb	\$2.252
a. SiCl ₄ required at stoichiometry, 100% efficiency, 13.13 lb	
b. 8% distillation loss, 1.335 lb	
c. 10% loss due to Si collection inefficiency, 1.459 lb	
d. 5% loss due to thermochemical inefficiencies and running slightly SiCl ₄ -rich, 0.768 lb	
2. Sodium metal, 8.033 lb/kg at \$0.1875/lb	1.506
a. Na required at stoichiometry, 100% efficiency, 7.23 lb	
b. 10% loss due to Si collection inefficiency, 0.803 lb	
3. Calcium hydroxide for waste disposal, 1.9 lb at \$0.015 lb	0.029
4. Argon, 4 SCF/kg at \$0.016/SCF	0.064
5. N ₂ , 7 SCF/kg at \$0.003/SCF	<u>0.021</u>
Raw materials cost, 1975 dollars	\$3.873
Raw materials cost, 1980 dollars	\$5.422

TABLE III
UTILITIES REQUIREMENTS

	<u>Cost/kg of Si</u>
1. Electricity, 9.06 kWh/kg at \$0.0342/kWh	\$0.310
a. Sodium (8.03 lb) vaporization at 90% efficiency, 6.15 kWh	
b. SiCl ₄ (15.36 lb) vaporization at 80% efficiency, 0.36 kWh	
c. Miscellaneous pumps, blowers, 2.0 kWh	
d. Sodium vapor delivery heaters, 0.05 kWh	
e. Reactor heaters (assumes using 2.8 kWh of heat generated by chemical reaction), 0.5 kWh	
2. Steam, 7.8 lb at \$0.00135/lb	0.0105
a. SiCl ₄ purification, 6.5 lb	
b. Caustic storage heater, 0.3 lb	
c. Na storage tanks, 1.0 lb	
3. Cooling water, 88 gal/kg at \$0.09/Mgal	0.6079
a. SiCl ₄ purification, 23 gal	
b. Reactor cooling, primarily NaCl condensation, 65 gal	
4. Process water, 16 gal/kg at \$0.405/Mgal	0.0065
a. Diluent for waste treatment, 16 gal	
5. Credit for 12 kWh of heat generated by condensing and cooling salt byproduct from 900°C to room temperature	---
Utilities cost, 1975 dollars	\$0.335
Utilities cost, 1980 dollars	\$0.469

taking the Battelle number multiplied by 0.68, the ratio of SiCl_4 flow through the AeroChem and Battelle SiCl_4 purification trains. The major questions regarding Table III are whether the large amount of heat released in the process can be put to use in the plant and what trade-offs are involved in the purchase of equipment which would allow this to be done. The process requires an electrical energy input of about 9 kWh/(kg of Si) with another 2.3 kWh/(kg of Si) needed in the form of steam. The total heat release from reacting and cooling the products to near room temperature is about 16.5 kWh/(kg of Si). Of this, in this analysis, we plan on using only the 2.8 kWh/(kg of Si) liberated chemically in the reactor to provide the major source of heat needed to maintain a reactor temperature of 1500°C. The major heat release (8 kWh) occurs when the NaCl vapor made in the reactor is condensed, a process which will occur at 800° to 900°C. The extent to which this high quality heat source can be used is uncertain. It needs a more detailed engineering work-up than we have been able to do to date. Therefore, here it has been conservatively assumed that it will not be used.

Labor costs are estimated assuming a total of six workers is needed; two workers are required to operate the SiCl_4 purification process, two to operate the reactors, one for product handling, and one for waste treatment. Since no workers are needed for electrolysis, our overall manpower requirement will be less than Battelle's.

For a first cut at getting major equipment costs we rely heavily on Table IIIA-1-5 of Yaws' 13th PIM presentation on the Battelle process. To get our costs we have modified this table as follows:

- a. The SiCl_4 purification train required (with associated scrubbers) is similar to Battelle's, but smaller. We have to purify 32% less SiCl_4 per kg of Si produced.* The costs of our equipment are thus scaled down using a factor $(1.00 - 0.32)^{0.6} = 0.79$.
- b. No SiCl_4 recovery from the reactor effluent is needed so no such equipment is included.
- c. No electrolysis-related equipment is required.

* This is in many respects a worst case assumption. The SiCl_4 purification train may be more extensive than needed if, for example, the heavy or light (or both) impurities tend to be separated out by the reaction and end up in the salt byproduct rather than in the silicon.

- d. No high-temperature heat exchanges to extract useful heat from molten NaCl are included in this analysis. Thus equipment corresponding to the Therminol system in the Battelle process is not included.
- e. We envision having 15 small 10 kg h^{-1} reactors* which produce Si, separate it from the NaCl at 90% efficiency, and produce $\approx 0.5 \text{ g}$ pellets of Si. The cost of each reactor is estimated to be about \$25,000 for a total reactor cost of \$375,000.
- f. The sodium metal vaporizer requires 0.84 MW. Battelle's zinc vaporizer requires 0.61 MW. A factor of $(0.84/0.61)^{0.6} = 1.21$ has been used to scale our costs to \$174,000 (from Battelle's \$144,000) for this item.
- g. Sodium storage facilities (50,000 gal at 100°C) are included at a cost of \$50,000 to hold a two-week supply of Na.
- h. Two 1000 cfm vacuum pumps are required at an estimated cost of \$50,000. (The second pump serves as a backup.) These pumps assume that the argon requirements are as large as shown in Table II. We believe this to be very conservative.

With these changes we obtain a cost for major process equipment of \$1,001,000 (1975 dollars) or \$1,414,000 (1980 dollars). The fixed capital investment is taken (from Yaws) to be $5.72 \times$ (major process equipment cost) or \$5,726,000 (1975 dollars) or \$8,016,000 (1980 dollars).

From the costs thus developed for raw materials, utilities, labor, and major process equipment, Table IV is obtained. A cost of silicon of $\$7.25 \text{ kg}^{-1}$ (1975 dollars) or $\$10.18 \text{ kg}^{-1}$ (1980 dollars) is projected.

* These small reactors would be slightly larger than one demonstrated in a 50 MT yr^{-1} unit. The conservative assumption has thus been made that no savings are realized by scale-up of the reactors in going from a 50 MT yr^{-1} unit to the 1000 MT yr^{-1} plant.

TABLE IV
TOTAL PRODUCT COST ESTIMATION

	<u>Cost/kg of Si</u>
1. Direct Manufacturing Cost (Direct Charges)	
a. Raw materials	\$3.873
b. Direct operating labor	0.290
c. Utilities	0.335
d. Supervision and clerical	0.043
e. Maintenance and repairs	0.573
f. Operating supplies	0.114
g. Laboratory charge	0.043
2. Indirect Manufacturing Cost	
a. Depreciation	0.573
b. Local taxes	0.114
c. Insurance	0.057
3. Plant Overhead	0.309
4. Byproduct Credit	---
4a. Total Manufacturing Cost (1 + 2 + 3 + 4)	\$6.305
5. General Expenses	
a. Administration	\$0.378
b. Distribution and sales	0.378
c. Research and development	0.189
6. Total Product Cost (1975 dollars)	\$ 7.27
Total Product Cost (1980 dollars)	\$10.18

III. PLANS

The new large capacity sodium vaporizer is now at an operational stage. This now permits the completion of the remaining tasks in this contract which are as follows:

- (i) The delivery of 0.25 kg silicon samples to JPL for evaluation.
- (ii) Investigation of impurities in the silicon samples.
- (iii) Measurement of heat release parameters from the reaction.

IV. NEW TECHNOLOGY

No reportable items of new technology were identified in this quarter.

V. REFERENCES

1. Miller, W.J., "Silicon Halide-Alkali Metal Flames as a Source of Solar Grade Silicon," First Quarterly Report, AeroChem TN-178, September 1977.
2. Miller, W.J., "Silicon Halide-Alkali Metal Flames as a Source of Solar Grade Silicon," Second Quarterly Report, AeroChem TN-182, December 1977.
3. Olson, D.B. and Miller, W.J., "Silicon Halide-Alkali Metal Flames as a Source of Solar Grade Silicon," Third Quarterly Report, AeroChem TN-187, ERDA/JPL 954777-78/3, March 1978.
4. Olson, D.B. and Miller, W.J., "Silicon Halide-Alkali Metal Flames as a Source of Solar Grade Silicon," Fourth Quarterly Report, AeroChem TN-192, DOE/JPL 954777-78/4, June 1978.
5. Olson, D.B. and Miller, W.J., "Silicon Halide-Alkali Metal Flames as a Source of Solar Grade Silicon," Fifth Quarterly Report, AeroChem TN-199, DOE/JPL 954777-78/5, October 1978.
6. Olson, D.B. and Gould, R.K., "Silicon Halide-Alkali Metal Flames as a Source of Solar Grade Silicon," Seventh Quarterly Report, AeroChem TN-205, DOE/JPL 954777-79/7, April 1979.
7. Dickson, C.R. and Gould, R.K., "Development of Processes for the Production of Solar Grade Silicon from Halides and Alkali Metals," First Quarterly Report, AeroChem TN-211, DOE/JPL 955491-80/1, February 1980.
8. Yaws, C.L. and Li, K-Y., "Process Feasibility Study in Support of Silicon Material Task I," Seventeenth Quarterly Report, DOE/JPL 954343-80/17, December 1979.